

## RAW MATERIALS

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### PYROPHYLLITIC RAW MATERIALS FROM THE KUL'-YURT-TAU DEPOSIT AS A BASE FOR CERAMIC COMPOSITES

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The physical-mechanical properties and the chemical and mineralogical compositions of pyrophyllitic rocks from the Kul'-Yurt-Tau deposit in the Republic of Bashkortostan were analyzed from the standpoint of using these materials as the principal component of the refractory composites based on a phosphate binder. The characteristics of the mineral pyrophyllite and surrounding rocks in the deposit indicated were examined. The initial materials for research were chosen on the basis of the information obtained.

**Key words:** pyrophyllite from the Kul'-Yurt-Tau deposit, composition, refractory composites, phosphate binder.

The use of the mineral pyrophyllite in the production of ceramics and refractories established a number of its valuable properties: good mechanical workability, high chemical stability, low content of alkali-metal oxides and coloring oxides, and others. Studies of such properties will make it possible to replace expensive conventional raw materials in mixes used for ceramic and refractory materials with pyrophyllitic material or to use it as an autonomous component for producing ceramics and refractories as well as other products [1, 2].

It should be noted that pyrophyllitic raw materials are widely used abroad in the ceramic and refractory industries. This is especially true in Japan, where until very recently roseki articles made of pyrophyllite have been the principal product of the refractory industry.

In the 1990s, in the USSR, up to 900 tons pyrophyllites per year of pyrophyllites were produced at the Ovruch deposits in Ukraine and used primarily for the production of heat-stable lighthouse and gas lamps. Manifold works have shown that pyrophyllite can in principle be used in the manufacture of a wide assortment of products. However, for a number of reasons, large-scale industrial processing still

does not exist; in the last ten years the production of pyrophyllites in Ukraine has stopped.

About 20 regions where pyrophyllite occurs in significant quantities have been found on the territory of the former USSR. Three deposits have been explored in detail; only preliminary surveys have been done at others. Exploration – assessments, geological surveys, and searches for other types of minerals have been performed at the remaining sites including at Kul'-Yurt-Tau, Gaiskoe, Mazarskoe, and Uzel'-kinskoe (Urals).

Pyrophyllitic raw material from the Kul'-Yurt-Tau deposit — the only deposit of pyrophyllite-bearing rock in the Republic of Bashkortostan that has been explored, is ready for operation, and is located next to consumers and the corresponding infrastructure — is located on the eastern slope of the Southern Urals 7 km north of the village of Baimak and 40 km west of the railroad station in Sibai. The geological data for this ore field have been described in detail by V. A. Prokin [6] and P. F. Sopko, et al. [7].

At the present time the Republic of Bashkortostan does not have its own resources for producing ceramic and refractory articles, while enterprises in the construction, machine building, and petrochemical industries have an urgent need for such articles. For this reason, one direction for the use of pyrophyllitic raw materials could be as the main component in refractory composites for fabricating the lining elements used in thermal furnaces for kilning ceramic brick, acid-resistant materials, and other products.

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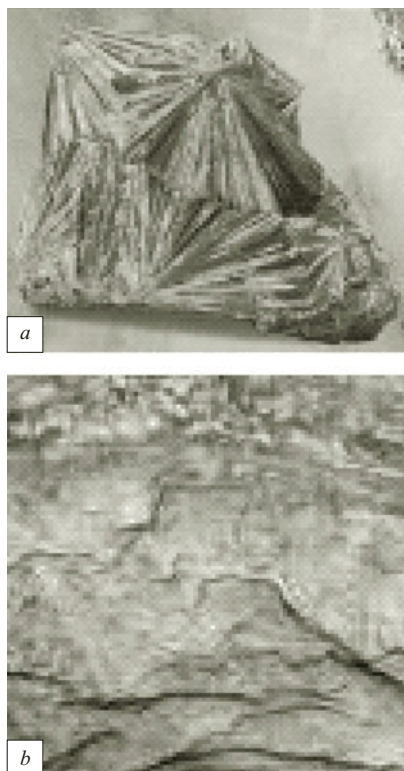


Fig. 1. View of the formations of primary pyrophyllite.

In the present article the pyrophyllitic raw material found in the Kul'-Yurt-Tau deposit is described from the standpoint using this material to produce refractory composites. This was preceded by an analysis of the published sources and data from laboratory research performed at the State Unitary Enterprise "BashNIISTROI" Institute [3–8]. Rocks which contain at least 85% pyrophyllite best meet the requirements of the refractory materials industry. The research performed by different authors made it possible to evaluate four types of pyrophyllitic raw material with respect to their applications in the refractories and ceramics industry: quartz-pyrophyllitic schists, sericite-pyrophyllite-quartz and sericite-pyrophyllitic schists with alkali content 1.5–4%; pyrophyllite-sericite schists and sericitolites with alkali content 4–9%; high-alumina quartz-pyrophyllite-diaspore rocks. All types are usable in the refractories industry.

**Principal Properties of Pyrophyllite.** Naturally occurring pyrophyllite (from the Greek  $\pi\upsilon\rho$  — fire and  $\phi\upsilon\lambda\lambda\omicron\nu$  — sheet) is a hydrated aluminosilicate with the chemical formula  $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$  and crystal-chemical formula  $\text{Al}_2(\text{Si}_2\text{O}_5)_2(\text{OH})_2$ . This mineral is grouped with clayey layered minerals (phyllosilicates) in accordance with the classification based on the crystallographic structure. Included are kaolinite, halloysite, pyrophyllite, montmorillonite, mica, and illite [9, 10]. Pyrophyllite differs from kaolin by a lower content of alumina and a higher content of silica; the theoretical composition of pyrophyllite is (wt.%)<sup>4</sup>: 66.7 SiO<sub>2</sub>,

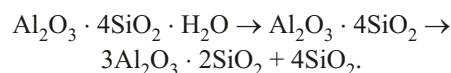
28.3 Al<sub>2</sub>O<sub>3</sub>, and 5 H<sub>2</sub>O. The crystal has a layered structure. The system is monoclinic, the symmetry prismatic, the cleavage along the (001) plane perfect, density 2.8–2.9 g/cm<sup>3</sup>, the fracture uneven, the color white sometimes with yellowish or greenish tinge; it is found in nature in the form of radiaxial (see Fig. 1) and continuous clusters (Fig. 1b).

The mineral is chemically inert with respect to strong acids and alkalis. This is due to the formation of protective films on the surface which prevent reagents from penetrating deep into the crystals during a reaction. For example, sulfuric acid decomposes pyrophyllite only with strong heating, while pyrophyllite hardly reacts at all with sulfuric and nitric acids.

The physical properties of pyrophyllite are practically identical to those of talc, since pyrophyllite has a similar structure in which magnesium is replaced with aluminum. For example, pyrophyllite is feels oily, has the same hardness and color, and sinters similarly on kilning [11, 12]. Pyrophyllite can be easily distinguished from talc by their reaction with cobalt nitrate  $\text{Co}(\text{NO}_3)_2$ : talc wetted with this reagent becomes red while pyrophyllite becomes blue [13].

The mineral appears colorless under a microscope; its luster is pearly and iridescent along cleavage surfaces; thin leaflets are transparent. The refractive indices of an optically biaxial crystal are  $N_g = 1.600$ ,  $N_m = 1.588$ , and  $N_p = 1.552$ . Pyrophyllite is synthesized artificially from silicon oxides and aluminum hydroxides (molecular ratio 4 : 1) at temperature 400°C and pressure 300 atm [13].

On heating the following transformations of pyrophyllite occur: water of constitution is completely removed in the interval 700–900°C; the product of complete dehydration is metapyrophyllite  $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ . At 1150°C metapyrophyllite decomposes with mullite and cristobalite being formed. The complete sequence of phase transformations of pyrophyllite on heating is



The final products of high-temperature transformations are refractory compounds — mullite and cristobalite — typical for all calcined aluminosilicates, kaolinite, kyanite, andalusite, sillimanite, topaz, and others. The phase transformations of pyrophyllite on kilning are elucidated in many works, though the parameters presented for the temperature intervals of the existence of the phases are quite contradictory.

In contrast to other naturally occurring aluminosilicates, the  $[\text{SiO}_2]$  and  $[\text{Al}(\text{O}, \text{OH})_6]$  groups in the structure of pyrophyllite are rigidly bound with one another. This is due to the wide interval of dehydration — 420–900°C [10, 11]. On heating to 1150°C it transforms into mullite and cristobalite, and in the process the hardness of its aggregates increases from 1–2 to 7–8 units on the Mohs scale. On heating to 1400°C the ultimate compression strength increases by almost an order of magnitude and reaches 210 MPa.

<sup>4</sup> Here and below, content by weight.

The metapyrophyllite formed after water is released retains the crystal structure and morphological indications of the initial material when heated to 1150°C. At the same time the authors of [11] concluded that chemically unstable metapyrophyllite transforms into a more stable phase — silica spinel at 1200°C, which undergoes disproportionation at 1300°C forming mullite and tridymite. However, according to other results, mullite formation in pyrophyllite occurs at temperatures from 1000 to 1100°C [10]. The reason for such an appreciable discrepancy in the data must be sought in the different chemical and phase compositions of the rocks in particular deposits.

The ambiguity of the interpretation of the mineral formation process occurring when pyrophyllite is kilned is explained by the nonequilibrium state of the samples even after prolonged (tens of hours) heat-treatment. Considering the limited capabilities of petrographic and x-ray analyses, the formation of mullite from intermediate anhydrite of the crystalline phase could not be confirmed and the conditions for the formation of a crystalline phase, whose crystal optical properties are close to those of keatite, could not be studied.

In summary, dehydration of pyrophyllite in the temperature interval 450 – 930°C occurs in two stages. This is due to different positions of the (OH)<sup>-</sup> groups in its structure. At temperatures above 1150°C metapyrophyllite decomposes, forming tridymite and mullite; above 1350°C tridymite transforms into cristobalite.

**Pyrophyllitic Rocks.** In nature the mineral pyrophyllite is rarely encountered in its pure form, while the rocks composed of it contain more or less amounts of the impurities kaolinite, alunite, sericite, feldspar, disthene, carbonates, and others. Deposits containing at least 50 – 75% pyrophyllite are of commercial interest. Generalizing all available general information from the geological standpoint and on the basis of the conditions of formation of the deposits, the authors of [14] divided them into five types; this classification is expounded in details in [3]. The types of deposits are determined by the altered rocks in the volcanogenic rock masses.

The pyrophyllitic raw material of this deposit can be divided as follows according to a complex of macro indicators, the microscopic and x-ray structural characteristics, and the particulars of the chemical composition of the rocks as a function of the content of alkalis and aluminum oxide:

- pyrophyllite-quartz low-alkali ( $K_2O + Na_2O = 0.2 - 0.4\%$ );
- sericite-pyrophyllite-quartz alkali ( $K_2O + Na_2O = 1.9 - 2.5\%$ );
- diaspore-sericite-pyrophyllitic high-alumina ( $Al_2O_3 = 38.0 - 45.6\%$ );
- pyrophyllitic alumina ( $Al_2O_3 = 26.7 - 28.6\%$ ).

All beds largely consist of pyrophyllite-quartz rocks. These are pyrophyllite-quartz and quartz-pyrophyllitic schists containing up to 10% sericite and on average 40 – 55% pyrophyllite. Sericite is present in amounts ranging from fractions of a percent to 45%; diaspore is encountered more rarely, its content varying from 5 to 45%. The amount

of quartz varies to 70%. On heating to 1400°C, the alkali varieties containing to 55% quartz as well as on average 25% sericite and 20% pyrophyllite form separate sections, interlayers, and lenses in the northern side of the quarry and outside its boundaries.

Pyrophyllite as a resource base for the production of refractory and ceramic articles has certain characteristics of the chemical composition of the surrounding rock. The technical conditions for it have not been determined, so that for a preliminary quality assessment it is desirable to take in consideration the industry requirements which have come together over many long years — the potential users of this resource. For the refractory and ceramic industries, the coloring oxide sum ( $Fe_2O_3 + FeO + TiO_2$ ) must not exceed 2.5%. Pyrophyllitic rocks containing no more than 0.7% of these components can be used as porcelain stones.

Because they lower the melting temperature of the glassy phase alkalis are harmful components for the production of refractory materials; the alkali sum must not exceed 1%. Raw material with at least 85% pyrophyllite best meets the requirements of the refractory materials industry. In this raw material the pyrophyllitic and quartz-pyrophyllitic rocks contain alkali-metal rocks from 0.1 to 1% with total coloring oxides 0.2 – 1.6%. The requirements of the ceramic industry are less stringent and make it possible to use the raw material from most deposits of the first and second types of rocks and sometimes of the third type also. Specifically, it is used for piecework production of gas and lighthouse lamps, radio parts, ceramic articles for different applications, and other articles. It is used to manufacture different kinds of fillers, because after comminution the rock must give a finely dispersed powdered material in the form of leaflets or flakes, which is achieved with (based on the experience gained in the talc industry) micaceous component content to 80 – 85%.

Judging from the publications, as a rule, technological studies in general touch upon a wide range properties but thorough studies are rarely done; usually, only some properties are determined. Specifically, pyrophyllitic rocks are usually replaced by one or another type of raw material in the mix of a specific ceramic or refractory material or introduced as an adjustment addition. In this connection, no systematic works on this problem have been found; usually, the principal technological properties of such materials are examined for specific examples.

Investigations of pyrophyllitic raw material and compositions based on it using phosphate binders are promising for practical applications. Such articles could find wide application in engineering for service at temperatures to 1200 – 1300°C because the raw material is inexpensive, the technology is simple and not energy intensive, and product quality is high.

Preliminary technological studies of Kul'-Yurt-Tau pyrophyllite deposit (Sibaiskii quarry in the Baimak region of the Republic of Bashkortostan) have made it possible to choose as the objects of study two forms of the most accessible and

**TABLE 1.** Oxide Content, %, of Pyrophyllitic Raw Material

Form of raw material	Oxide content, %, of pyrophyllitic raw material							
	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O + K <sub>2</sub> O	other
PP	66.95	0.77	25.07	0.57	0.14	0.06	2.22	4.8
PPS	51.96	0.95	37.80	0.05	0.28	0.10	0.68	7.5
QPPS	81.80	—	14.22	—	0.35	0.45	1.01	2.5

abundant quarry raw materials — quartz-pyrophyllitic schists (QPPS) and quartz-pyrophyllite-diaspore rock (PPS).

The Mozyr'-Ovruchskoe pyrophyllite (PP), being the technologically most thoroughly studied raw material, was used to obtain comparative data. The chemical composition of the initial pyrophyllitic rocks is presented in Table 1. The mineralogical composition of the pyrophyllite is presented in Table 2.

As microscopic studies have shown, chunks of pyrophyllite rock (no inclusions) consist of small prolate flakes; small aggregates (to 2 mm in size) of finely flaked kaolinite and single grains of diaspore are only rarely encountered. Its chemical composition fluctuates in the following ranges: 48.24 – 48.44 SiO<sub>2</sub>; 41.3 – 41.83 Al<sub>2</sub>O<sub>3</sub>; 1.10 – 1.15 Fe<sub>2</sub>O<sub>3</sub>; 0.56 – 0.65 CaO; 0.10 – 0.12 MgO; 7.8 – 7.79 other.

Pyrophyllitic schists contain, aside from quartz and pyrophyllite, sericite, and for this reason they are characterized by a complex structure. Both schist pyrophyllite-sericite or sericite varieties with quartz impurity to 5% and rocks with a more massive constitution with pyrophyllite-sericite-quartz compositions (the quantitative ratio of pyrophyllite, sericite, quartz on average is 1:1:3, the average content is 83.7 SiO<sub>2</sub> and 9.3 Al<sub>2</sub>O<sub>3</sub>) with brecciate or spotty texture, due to a nonuniform distribution of quartz and micaceous components, are present in the samples.

On a microscopic level the initial quartz-pyrophyllitic raw material is characterized by a combination of two textured varieties. The first one is brecciate with clear predominance of disintegrated quartz, a heterogranoblastic aggregate against whose background formations of a second phase — amoeboid, ribbon-like, or lenticular (about 0.6 – 1.5 mm in size) — are visible; they consist of a pyrophyllite-sericite

lepidoblastic mass, unidirectional orientation being uncharacteristic for these sections.

Ordinarily, the size of the individual flakes of pyrophyllite does not exceed 0.008 mm. Larger, individual, sericite flakes reach 0.01 – 0.02 mm in length. The quantitative ratio of sericite and pyrophyllite fluctuates from 1:2 to 1.5:1. Blastopyrophyllitic quartz segregations are encountered only rarely (in amounts no greater than 5%); their average size is 2 – 2.5 mm. Ordinarily, they are rounded or isometric with resorbed edges. They are subjected to partial granulation.

Under a microscope pyrophyllite-sericite and sericite schists appear to be a uniform oriented mass with lepidoblastic structure; the pyrophyllite content fluctuates from 0 to 35%. Individual quartz grains 0.8 – 1 mm in size or their aggregates, whose amount does not exceed 3 – 5% of the total volume of the rock, are encountered, but only rarely, in this schist mass.

The results of a generalization of the published data and preliminary studies show that phosphate compositions based on orthophosphoric acid (OPA), when stored in air with no preliminary heat treatment, accumulate moisture because of the hygroscopicity of phosphates and the acid itself. In this system the acid still interacts only weakly with the powdered components to temperature 110°C. The samples lose most of their water when heated to 400°C, while when other forms of phosphate binders are used the heating temperature is 200°C. As a result of the water being removed the mechanisms of solidification with formation of hydrogen bonds at temperatures 180 – 220°C weaken, and with further heating to 300°C they decrease considerably. For purposes of obtaining compositions which are stable in air they must be heat-treated at 400 – 500°C.

## CONCLUSIONS

Judging from the published data and the preliminary research done at the State Unitary Enterprise “BashNIISTroi” Institute, pyrophyllitic rocks are a very promising, local, natural, raw material for producing ceramic and refractory objects. With respect to their properties they are close to the previously used raw material from the Ovruch deposit. Analysis of the technical properties of rocks from the Kul'-Yurt-Tau deposit shows that they can be used as a basis for manufacturing refractory composites with a phosphate binder.

**TABLE 2.** Mineralogical Composition of Pyrophyllite Raw Material

Mineral	Content, wt. %		
	PP	PPS	QPPS
Pyrophyllite	72 – 74	62 – 64	34 – 36
Kaolinite	3 – 4	10 – 12	2 – 3
Quartz	24 – 25	0.2 – 0.5	46 – 48
Diaspore	1 – 2	11 – 12	1 – 2
Sericite	3 – 4	2 – 3	3 – 4



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